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M. Boyet, R. W. Carlson, L. E. Borg, M. Horan

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Sm-Nd systematics of lunar ferroan anorthositic suite rocks: Constraints on lunar crust formation

Maud Boyet[1], Richard W. Carlson[2], Lars E. Borg[3] and Mary Horan[2]

[1]Clermont Université, Université Blaise Pascal, Laboratoire Magmas et Volcans, UMR 6524, 5 rue Kessler 63038 Clermont-Ferrand, France.
M.Boyet@opgc.univ-bpclermont.fr Tel: +33(0)4.73.34.67.35

[2]Department of Terrestrial Magnetism 5241 Broad Branch Road, NW Washington, DC 20015-1305 USA.
rcarlson@ciw.edu Tel. (202) 478-8474
mhoran@ciw.edu Tel. (202) 478-8481

[3]Chemical Sciences Division, Lawrence Livermore National Laboratory, 7000 East Avenue L-231, Livermore CA 94550 USA.
borg5@llnl.gov Tel. (925) 424-5722

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Abstract

We have measured Sm-Nd systematics including the short-lived ^{146}Sm-^{142}Nd chronometer in lunar ferroan anorthositic suite (FAS) whole rocks (15415, 62236, 62255, 65315, 60025) with at least some members of the suite thought to be primary crystallization products formed by plagioclase flotation during crystallization of the lunar magma ocean (LMO). Most of these samples, except 62236, have not been exposed to galactic cosmic rays for a long period and thus require minimal correction to their ^{142}Nd isotope composition. These samples all have measured deficits in ^{142}Nd relative to the JNdi-1 terrestrial standard in the range -45 to -21 ppm. The range is -45 to -15 ppm once the 62236 ^{142}Nd/^{144}Nd ratio is corrected from neutron-capture effects. Analyzed FAS samples do not define a single isochron in either ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd systematics, suggesting that they either do not have the same crystallization age, come from different sources, or have suffered isotopic disturbance. Because the age is not known for some samples, we explore the implications of their initial isotopic compositions for crystallization ages in the range of 50-300 Ma after the beginning of accretion, a timing interval that covers all the ages determined for the ferroan anorthositic suite whole rocks as well as different estimates for the crystallization of the LMO. 62255 has the largest deficit in ^{142}Nd and does not appear to have followed the same differentiation path as the other FAS samples. The large deficit in ^{142}Nd of FAN 62255 may suggest a crystallization age around 60-100 Ma after the beginning of solar system accretion. This result provides essential information about the age of the giant impact forming the Moon. The initial Nd isotopic compositions of FAS samples can be matched either with a bulk-Moon with chondritic Sm/Nd ratio but enstatite-chondrite-like initial ^{142}Nd/^{144}Nd (e.g. 10 ppm below modern terrestrial), or a bulk-Moon with superchondritic Sm/Nd ratio and initial ^{142}Nd/^{144}Nd similar to ordinary chondrites.

1. Introduction

Rocks from the lunar highlands are divided into two main sample suites, the ferroan anorthosite suite defined by Dowty et al. (Dowty et al., 1974) and the magnesium-rich plutonic suite (Warner et al., 1976). Four ferroan anothosite (FAN) subgroups were defined by James et al. (1989) on the basis of their modes and mineral compositions. The ferroan anorthosites sensu stricto are composed of at least 90% plagioclase. Both petrographic and geochemical studies of FAS rocks suggest their derivation through crystallization from a single evolving magma, but no single petrogenetic model consistently explains all the characteristics of the various members of the FAS (e.g. (Floss et al., 1998; Haskin et al., 1981; James et al., 1989; Steele and Smith, 1973). Smith et al. (Smith et al., 1970). Wood et al. (Wood et al., 1970) were the first to suggest that anorthositic rocks could be remnants of the earliest lunar crust formed by crystal fractionation and plagioclase flotation during the crystallization of the lunar magma ocean (LMO). Crystallization of the LMO is predicted to have produced distinct chemical reservoirs with dense mafic cumulates that later became the source of mare basalts, whereas the last liquid to solidify at the end of the crystallization would be enriched in incompatible elements and sampled by the KREEP basalts (enriched in K, rare earth elements (REEs) and P).

The age of the Moon is an old debate and different approaches have been considered for dating the giant impact that formed the Moon. Accretion of the Moon from the impact-generated disk around Earth is a very short process ($<10^3$ years, (Pahlevan and Stevenson, 2007)). Since the LMO would crystallize very rapidly until the lunar crust formed (in less than a million years, (Elkins-Tanton et al., 2011; Solomatov, 2000), the age of earliest lunar crust can be estimated by dating the FAS rocks. Dating these sample is challenging because they do not contain zircons and thus cannot be dated easily by U-Th-Pb systematics. They are essentially monomineralic plagioclase and in this case the dating by isochron method is compromised. Finally they are often brecciated due to the long exposure of the lunar crust to meteorite bombardment and shock metamorphism may have disturbed their radiometric systems. Two samples from the FAS provide concordant ages from multiple isotope dating techniques. Sample 60025 was dated at 4360±3 Ma using the ^{207}Pb-^{206}Pb, ^{147}Sm-^{143}Nd and ^{146}Sm-^{142}Nd isotope systems (Borg et al., 2011) and an age of 4470±70 Ma was reported for 67075

using Rb-Sr and ^{147}Sm-^{143}Nd isochron methods (Nyquist et al., 2010). These samples do not belong the FAN group sensu stricto. FAN 60025 belongs to the mafic magnesian (MM) subgroup that contains more abundant mafic minerals. FAN 67075 is a feldspathic fragmental breccia that would be classified in the FAN group, however this sample contains REE concentrations that are 2 to 4 times higher than typical FANs.

Coupled ^{142}Nd-^{143}Nd isotope systematics of lunar low-Ti and high-Ti mare basalts along with KREEP basalts have been used to constrain the age of crystallization of the lunar interior (Boyet and Carlson, 2007; Brandon et al., 2009; McLeod et al., 2014; Nyquist et al., 1995; Rankenburg et al., 2006) . These studies demonstrate that the Sm-Nd systematics in the lunar mantle closed in the interval of 180-250 Ma after the beginning of solar system formation, depending on the model considered for lunar mantle differentiation. This age is consistent with the most recent results obtained on ^{182}Hf-^{182}W ($T_{1/2}$ = 8.9 Ma, (Vockenhuber et al., 2004) systematics measured on metals from lunar basalts and pure plagioclase separates from ferroan anorthosites that demonstrate no evidence for live ^{182}Hf when the different lunar geochemical reservoirs formed (Touboul et al., 2007 ; Touboul et al., 2009). A prolonged lunar magma ocean crystallization interval might be expected given the insulating effect of the thick plagioclase crust (Solomon and Longhi, 1977), so closure of the Sm-Nd systematics in the lunar mantle, particularly in a late stage LMO component like KREEP, might substantially post-date the anorthositic crust formation. Moreover, dating the lunar interior using the planetary isochron method, involves many assumptions about the petrogenetic history of the samples used to define the isochron, and several alternative models have been proposed. These models call into question the chronological significance of a whole-rock isochron since various processes may have affected the lunar mantle early in its history including cumulate overturn (e.g. (Parmentier et al., 2002) and tidal heating/melting (Meyer et al., 2010). Bourdon et al. (Bourdon et al., 2008) reproduce this ~200 Ma ^{146}Sm-^{142}Nd "age" by a fractionation-mixing model running for 350 Ma. As the slope of the Sm/Nd-^{142}Nd/^{144}Nd correlation line is strongly influenced by the high-Ti basalts which have the highest Sm/Nd ratios, Carlson and Boyet (Carlson and Boyet, 2009) noted that a late formation of this source reservoir would significantly modify the slope of the regression line leading to an apparent age without geological meaning.

In order to provide more constraints on the timing of lunar crustal evolution and discuss the age of Moon formation, we have measured the ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd systematics in several FAS whole rock samples of (15145, 60025, 62236, 62255, and 65315). Unfortunately not all of these samples have reliable crystallization ages because several are composed almost purely of plagioclase. Nevertheless, the $^{142-143}$Nd isotopic composition of bulk samples can provide information on the early evolution of the Moon.

2. Sample description

Five samples from the FAS have been measured for Sm-Nd isotopic composition in this investigation. Four of them were collected during the Apollo 16 mission that landed in the Descartes region (60025, 62236, 62255, and 65315). Sample 15415 was collected in a different region close to the Imbrium Basin. It is the only FAN collected at the Apollo 15 site. Although this sample is often deemed to be pristine and minimally affected by impact, its geographic position suggests that it has been ejected from an impact into the lunar highlands. Pristine, in this context means only that the sample has low abundances of highly siderophile elements implying that it does not contain a meteoritic component contributed by impact.

Following the subgroups defined by James (1980), samples 60025, 62255 and 65315 are coarse-grained granular rocks. 62236 has experienced a more intense recrystallization and belongs to the medium-grained granoblastic rocks. A detailed sample description of all the samples studied here can be found in the Lunar Sample Compendium. Most of FAS samples are breccias. Samples 62255 and 65315 are diamict breccias with two different lithologies: cataclastic anorthosite and clast-poor impact-melt rock (James 1981). Sample 62255 is composed of 65% prisitine anorthosite and 35% impact melt. Sample 65315 is described as a cataclastic anorthosite with a glass coating. The two analyzed fragments for samples 62255 and 65315 were selected from the anorthosite-dominated parts of the samples. Once ground, the splits analyzed were thoroughly examined under binocular microscope and found to contain nothing but anorthite. Sample 15415 is described as a pristine coarse-grained unbrecciated

anorthosite composed of up to 98% plagioclase. The selected piece of 60025 was chosen because it was enriched in mafic minerals (about 25% of olivine and pyroxene) that allowed an internal ^{146,147}Sm-^{142,143}Nd isochron to be defined (Borg et al., 2011). The whole-rock fraction is essentially composed of plagioclase as shown by the Sm-Nd isotope similarity between this whole-rock measurement and that of the plagioclase separate (Borg et al., 2011). Sample 62236 is a noritic ferroan anorthosite that contains higher abundances of mafic minerals than typical FANs. In the compilation of modes for pristine FAS presented in Warren (1990) we note that 62236 and 60025 contain 17.5 and 12.6 wt% of mafic minerals respectively and are classified into the mafic magnesian (MM) subgroup. These rocks have more abundant mafic minerals and they are more magnesian in composition than sensu-stricto FANs. All other samples analyzed in this study are typical ferroan anorthosites with plagioclase abundances up to 99.5%. Plagioclase compositions in FANs and in samples from the MM subgroup are similarFANs have the lowest REE abundances of any samples from the lunar crust due to the very low partition coefficients of these elements in plagioclase (except for Eu that is compatible under the 2+ valence state). Samples analyzed in this study are all poor in REE indicating that are mainly composed of plagioclase and have not undergone metasomatism, or contamination by a KREEP-rich source.

3. Analytical techniques

3.1. Sm-Nd separation

Samples were analyzed during two different periods called series 1 and 2 in the Table 2. Because the REE contents are very low in FAS rocks (Nd<250 ppb), large samples must be dissolved to allow high precision Nd isotope measurements (Table 2). Samples 15415, 62255, and 65315 were analyzed during session one. Four different isotope measurements were done: both Nd and Sm isotopic composition of unspiked fractions and Nd and Sm isotopic composition of spiked fractions for measuring the Sm/Nd ratio by isotope dilution. Samples 60025 and 62236 were analyzed during the second session. For these samples, a very pure ^{150}Nd spike (99.99%) was used whose level of isotopic enrichment was such that the samples could be total-spiked because the

corrections to ^{142}Nd from the spike were negligible. Moreover, the unspiked Sm isotope compositions had already been determined on these two samples (Borg et al., 1999 ; Boyet and Carlson, 2007; Carlson and Lugmair, 1988).

A first set of experiments were performed on a terrestrial anorthosite before starting the series 1 lunar sample dissolution. We experienced difficulty in correctly measuring the Sm/Nd ratio on a small aliquot when the sample was dissolved using the common acid digestion technique (mixture of concentrated HF and HNO_3 acids in sealed beakers placed on a hot-plate for 48 hours – identified as method 1 in figure 1). The Sm/Nd ratios obtained on separate dissolutions of the same sample powder using method 1 were not reproducible and always lower than those obtained using the fusion technique (methods 2 and 3 in figure 1). After HF-HNO_3 dissolution, we could not obtain a clear solution in HCl when the aliquot to be spiked was taken. We suspect that a small amount of precipitate is the cause of the Sm/Nd fractionation. The same sample powder was dissolved by fusion with a mixed Li-metaborate/tetraborate fluxing agent and two tests were undertaken. The mixed Sm-Nd spike was added before (method 2) and after (method 3) the REE were co-precipitated with Fe. The co-precipitation occurred at pH 5.5 (adjusted with ammonia) by adding a small quantity of Fe to the sample because the natural iron content in these samples was too low for efficient Fe precipitation. Identical $^{143}Nd/^{144}Nd$ ratios were measured for both splits and they are equal to the ratio measured when the sample was unspiked and dissolved by the fusion technique (result not shown here). However, the measured $^{147}Sm/^{144}Nd$ ratios were not reproducible when the spike was added after the co-precipitation with Fe. On the basis of these results on the terrestrial anorthosite, samples 15415, 62255, and 65315 were processed following method 2. After the fusion step and once completely dissolved in 2M HNO_3, 10% of the sample solution was taken and spiked with a mixed ^{149}Sm-^{150}Nd tracer. Then, REE were co-precipitated. From the precipitate, Sm and Nd were separated using two different columns and a chemistry procedure almost identical to that described in (Boyet and Carlson, 2005). REE are first separated on a cation resin using HCl and then Nd and Sm are separated from other REE on a 20-cm long cation resin column using 2 methylactic acid. Due to the large sample size, the amount of flux used is important. The total analytical blank using 5 g Li-metaborate and 1 g sample is 3 ng for Nd and 0.6 ng for Sm. The uncertainty on the blank estimated from two repeated measurements is less

than about 10%. The isotope composition has been determined during the same measurements on the Triton. Although the isotope composition of the blank requires large correction due to the spike contribution, we measured the blank 143Nd/144Nd=0.5014±0.005. The blank correction changes the $^{147}Sm/^{144}Nd$ ratio of samples 15415, 62255, and 65315 by about 1% and the correction is negligible on the Nd isotope ratios.

The analytical method was changed for the second set of experiments for FANs 62236 and 60025. For these samples, a very pure ^{150}Nd spike (99.99%) was used whose level of isotopic enrichment was such that the samples could be total-spiked because the corrections to ^{142}Nd from the spike were negligible. The mixed ^{150}Nd-^{149}Sm spike was added before the dissolution procedure that used a mixture of concentrated ultra pure HF and HNO_3 acids. Complete dissolution of such large, plagioclase-rich, samples requires very large acid volumes (e.g. 300 ml 6M HCl for 62236). The chemistry follows the Sm-Nd separation developed by Boyet and Carlson (Boyet and Carlson, 2005). However due to the large sample size, each sample was split into 6 aliquots and loaded onto separate first cation columns. The REE split from each column was then combined for further Nd purification on a 2-methylactic column. The Sm and Nd blank following this procedure is 0.3 ng and 1 ng, respectively, for 1 g of sample dissolved. Blank corrections have been applied to the measured data but can be considered negligible as they are lower than the analytical precision.

3.2. Isotope measurements

Isotope measurements were performed on the DTM Triton (Thermo Fisher thermal-ionization mass spectrometer). Nd and Sm were loaded on zone-refined Re filaments and measured in metal form. Sm isotope measurements were performed in static mode. Nd and Gd interferences were monitored on masses 146 and 155, respectively. For samples that have been exposed to cosmic rays for a significant period of time, the unspiked Sm isotope composition must be measured. When the Sm isotope compositions were available in the literature, these measurements were not redone (60025 and 62236). Results obtained using two different Sm isotope ratios for the mass

bias correction are presented in Table 1. Sm isotope composition is normally corrected to $^{147}Sm/^{152}Sm=0.56081$, however this data correction can be compromised for samples enriched in Eu, which is the case for FAS rocks. ^{152}Eu is produced by thermal neutron addition to ^{151}Eu, and decays to ^{152}Sm in a few tens of years. For this reason, data are also presented in Table 1 using the normalization ratio $^{148}Sm/^{154}Sm=0.49419$. The external precision determined on the repeated measurement of the standard Sm using both normalization ratios is similar (≈ 20 ppm on ^{149}Sm and ^{150}Sm isotope ratios). The external reproducibility has been estimated from repeated measurements of the Sm terrestrial standard (n=4). The same range of precision was obtained on the DTM Triton during previous isotope studies in which more standards were measured (Boyet and Carlson, 2007 ; Carlson et al., 2007).

For Nd isotope measurements, a two-step multicollector scheme was used that allowed the determination of the $^{142}Nd/^{144}Nd$ dynamically whereas all other ratios are determined statically on the same acquisition line. Faraday cups are centered successively on masses 145 and 143 and the $^{142}Nd/^{144}Nd$ ratios measured on the second line are corrected using the $^{146}Nd/^{144}Nd$ ratios measured on the first line. Isotope ratios determined in static routine are corrected using the $^{146}Nd/^{144}Nd$ ratio measured in the same line using an exponential law and a $^{146}Nd/^{144}Nd$ ratio equal to 0.7219. The quality of the Nd chemical separation is monitored by measuring ^{140}Ce and ^{147}Sm on L4 and H2 Faraday cups, respectively. The external precision is defined by repeated runs of the JNdi-1 terrestrial standard. We obtained an average $^{142}Nd/^{144}Nd$ ratio of 1.141837 during the two sessions with a precision better than 6 ppm (Table 2). $^{143}Nd/^{144}Nd$ ratios measured on the JNdi-1 isotope standard are equal to 0.512109±3 (n=3) and 0.512112±2 (n=6) for sessions 1 and 2, respectively (Table 2). This value is in agreement with the reference value for this standard (0.512115±7 (Tanaka et al., 2000). Each measurement consists of 27 cycles of 20 ratios (8s integration). For FAS samples, the runs were shorter due to the lower quantity of Nd loaded (Table 2).

4. Results

4.1. Sm isotope data and neutron capture correction

Because the lunar surface is exposed to galactic cosmic rays, the Sm and Nd isotopic composition of lunar rocks can be modified by secondary neutron capture. The isotopic composition of Sm is used to correct Nd isotope composition when an extended exposure history is identified. The isotope ^{149}Sm is used as a basis for this correction because it has the largest neutron capture cross section of all Sm and Nd isotopes. As explained in the previous section, Sm isotope compositions have been determined for samples 15415, 62255 and 65315, whereas samples 60025 and 62236 were measured previously by (Boyet and Carlson, 2007) and (Borg et al., 1999) respectively. The Sm isotope composition of 60025 is normal (Boyet and Carlson, 2007) and the two fragments of 62236 analyzed by Borg et al. (1999) and during this study are derived from ~10 cm of one another so even if the neutron fluence effect is depth dependant, we can reasonably assume that the two aliquots share a common Sm isotope composition. The Sm isotope results are presented using two different normalization schemes, ^{147}Sm/^{152}Sm=0.56081 and ^{148}Sm/^{154}Sm=0.49419 in Table 1. Results are compared in figure 2 and previous data obtained on mare basalts using the same instrument are also presented (Boyet and Carlson, 2007). For mare basalts, the same ε^{149}Sm and ε^{150}Sm values are determined using either normalization scheme. In contrast to FAS rocks, mare basalts tend to be depleted in Eu relative to other REE. In FAN samples, the choice of normalization ratio is important as shown by sample 15415 in figure 2A, because of the significant production of ^{152}Sm by neutron capture by ^{151}Eu. The Sm isotope composition calculated using ^{147}Sm/^{152}Sm for fractionation correction does not lie on the ε^{149}Sm- ε^{150}Sm correlation line. FAN 62236 is strongly affected by neutron capture (ε^{149}Sm=-31; Borg et al., 1999), 15415 is only slightly affected by neutron capture (ε^{149}Sm=-15), and the 3 other FAS rocks (60025, 62255, and 65315) have terrestrial ^{149}Sm and ^{150}Sm abundances.

The Nd isotope ratios of samples exposed to large neutron fluences also are modified by neutron capture. Two different correction schemes have been proposed based on different estimates of the ^{149}Sm capture cross section: 41,000 barns (Lingenfelter et al., 1972 ; Nyquist et al., 1995) and 71,627 barns (Rankenburg et al., 2006). The difference in the magnitude of the correction to ^{142}Nd/^{144}Nd ratios changes

by a few ppm depending on which cross section is used (figure 2B). The y-axis on figure 2B represents the magnitude of the correction on the $^{142}Nd/^{144}Nd$ ratio relative to the exposure ages of the samples. For sample 62236, which is in this study the sample the most affected by neutron capture, the method of correction changes the final $^{142}Nd/^{144}Nd$ ratio by 12 ppm. This is the only sample for which the difference is higher than the analytical precision defined by replicate analyses on Nd standards (error bar represented in Figure 2B). We decided to present results obtained from the correction method developed by Rankenburg et al. (Rankenburg et al., 2006) in Table 2 because this method uses the most recent data available for neutron capture cross sections of Sm and Nd isotopes. Moreover the quality of the correction has been thoroughly examined by looking at the $^{145}Nd/^{144}Nd$ ratios of the same lunar samples (Brandon et al., 2009). The ^{145}Nd isotope is the most affected by large neutron fluxes. The method developed by Rankenburg et al. (Rankenburg et al., 2006) and Brandon et al. (Brandon et al., 2009) can reproduce terrestrial $^{145}Nd/^{144}Nd$ ratios in samples with significant neutron capture histories where uncorrected ratios change by about 30 ppm for the most affected samples (see results from Model 1, Table 5 in (Brandon et al., 2009). The $^{145}Nd/^{144}Nd$ ratios are presented in Table 2. We note that all samples show a terrestrial $^{145}Nd/^{144}Nd$ ratio within error whereas a small deficit in $\mu^{145}Nd$ is expected for sample 62236 ($\mu^{145}Nd$ of 0.8 ± 3.9 ppm, mean of the 2 measurements). For comparison the KREEP sample 15386 that has a ^{149}Sm deficit similar to that of 62236 has a deficit in $\mu^{145}Nd$ of -15±4 ppm (Brandon et al., 2009).

4.2. Sm-Nd systematics

The samples in this study were measured during two analytical sessions separated by an interval of one year. The Nd isotope ratios measured in static mode did not change over this time interval. In the configuration used, $^{142}Nd/^{144}Nd$ ratios are determined in both static and dynamic modes (Table 2). All static and dynamic ratio measurements are in good agreement, except for the sample 65315 (Figure 3). This sample produced very low signal intensity that declined continuously during a short run of 180 ratios. Given these concerns over data quality for 65315, we will not consider the $^{142}Nd/^{144}Nd$ ratio measured for this sample in the discussion.

All FAS rocks have $^{147}Sm/^{144}Nd$ ratios lower than 0.16, except for 62236 that has a ratio of 0.1768. This sample has the highest $^{143}Nd/^{144}Nd$ ratio and the lowest deficit in ^{142}Nd (-15 ppm, average of two measurements) relative to the terrestrial standard. All other FAS rocks have $^{143}Nd/^{144}Nd$ ratios in the range of 0.511323 to 0.511542 and $^{142}Nd/^{144}Nd$ ratios between -45 to -26 ppm relative to the terrestrial standard. Data obtained for 60025 on the DTM Triton in 2007 can be compared to our more recent measurement. The $^{142}Nd/^{144}Nd$ ratios measured in these two fractions are identical within error ($\mu^{142}Nd$= -21±7 and -26±13 in Boyet and Carlson (2007) and in this study, respectively) however $^{143}Nd/^{144}Nd$ ratios are different. A ratio of 0.511542 was measured in the current study (data published in Borg et al., 2011) while we measured a ratio of 0.511348 in a previous study (Boyet and Carlson, 2007). We did not determine the $^{147}Sm/^{144}Nd$ ratio in 2007 due to analytical problems with sample dissolution. The difference in measured $^{143}Nd/^{144}Nd$ ratios could reflect a small variation of $^{147}Sm/^{144}Nd$ ratio in the different whole rock aliquots. Considering the ^{147}Sm-^{143}Nd isochron of Borg et al. (2011), we estimate a Sm/Nd ratio of 0.1519 for the bulk rock sample analyzed in 2007 (a correction on the $^{143}Nd/^{144}Nd$ ratio has been applied to our 2007 results since the mean obtained on the JNdi-1 standard during this period of measurement was 0.512119±6 for n=3 in 2007). A change of Sm/Nd ratio of this magnitude would have only a minor effect on the $^{142}Nd/^{144}Nd$ ratio because at 4.36 Ga, the age of crystallization of 60025, ^{146}Sm has already largely decayed to ^{142}Nd. The calculated initial $^{142}Nd/^{144}Nd$ ratio would change by less than 5 ppm. The long-term evolution of FAS rocks with sub-chondritic Sm/Nd ratios produces $^{143}Nd/^{144}Nd$ ratios lower than the chondritic ratio (0.512630; (Bouvier et al., 2008).

Our data for 62236 are not similar to those measured on the same sample by Borg et al. in 1999. We measure a large deficit in ^{142}Nd relative to the terrestrial standard (average of the two measurements: $\mu^{142}Nd$ of -31.9±3.5 ppm) whereas they analyzed two different fractions of this sample and measured small ^{142}Nd deficits of -4±12 ppm and -2±25 ppm. Results obtained on the ^{147}Sm-^{143}Nd systematics are also slightly different. Our WR measurement falls slightly to the right of their isochron (Figure 4). We note that the Borg et al. whole rock data for 62236 were obtained on 27 mg sample sizes (< 5 ng Nd) using NdO+ whereas our measurement used 2.78 grams of

sample. The quantity of Nd measured is more than 100 times higher and was measured using the Nd metal ion, thus eliminating the need for correction for oxygen isotopes. The explanation for this shift remains unclear, however, a small effect coming from the spike calibration or the blank correction in the first study is suspected. The initial $^{143}Nd/^{144}Nd$ ratios expressed in epsilon notation and calculated back to the Sm-Nd isochron age of 4.29 Ga (Borg et al., 1999) changes from +3.1 (Borg et al., 1999) to +0.62 for the data in this study.

5. Discussion

5.1. Age of FAS rocks

Among the FAS rocks analyzed here, only two samples have been dated using Sm-Nd systematics. Borg et al. (2011) published an age of 4.360±0.003 Ga for 60025. For the first time for a lunar FAS rock, the same age was obtained for one sample by 3 different chronometers (Pb-Pb and ^{146}Sm-^{142}Nd, ^{147}Sm-^{143}Nd). This age is younger than the previous ^{147}Sm-^{143}Nd age determination obtained on the same sample (Carlson and Lugmair, 1988). Although the Carlson and Lugmair (1988) isochron was based on a larger number of analyzed fractions and larger spread in Sm/Nd ratios of the separated mineral fractions, the quantity of Nd analyzed was low (from 1.5 to 20 ng with all mafic phases below 6 ng Nd) and was measured as the NdO+ ion. Compared to the techniques used here, the Carlson and Lugmair (1988) data required corrections for both the O isotope composition and a larger blank contribution. Borg et al. (2011) noted that if the blank contribution is doubled, both age determinations are identical within error. Sample 62236 was dated at 4.29±0.06 Ga by internal ^{147}Sm-^{143}Nd isochron (Borg et al., 1999). As discussed in the previous section, several reasons (spike calibration, blank contribution, sample size), can be invoked to explain the small discrepancy between our measurement of the 62236 whole rock and those of Borg et al. (1999). Our data suggest a significantly lower initial $\varepsilon^{143}Nd$ and measured $\varepsilon^{142}Nd$ when calculated relative to the JNdi standard ratio (+0.62 and -0.32 epsilon, respectively) compared to the values published in Borg et al. (1999) (+3.1 and +0.03 epsilon, respectively) at the 4.29 Ga age determined by Borg et al. (1999). The difference between our whole rock 62236 data

and that measured by Borg et al. (1999) also introduces the question of the accuracy of the surprisingly young age.

When all our FAS WR data are plotted on a $^{147}Sm/^{144}Nd$ vs $^{143}Nd/^{144}Nd$ isochron diagram they define a scattered array with a best-fit slope yielding an unrealistic old age of 4.90±0.27 Ga (MSWD=8.3) (Fig 5). The regression line is strongly controlled by 62236, because all the other FAS whole rocks measured here have very similar Sm/Nd ratios with a range of only 5%. When this sample is not included in the regression, the slope of the line is even steeper, however, the very small range of Sm/Nd ratios yields an imprecise slope corresponding to very imprecise age of 4.9 ±1.6 Ga with an uncertainty large enough to encompass any reasonable age for the FAS rocks. The ^{147}Sm-^{143}Nd isotope compositions of samples 15415, 62255 and 65315 do not fall on the 60025 Sm-Nd internal isochron. Either these samples do not come from the same reservoir and/or were not formed at the same time as 60025. Moreover the intense meteorite bombardment occurring during the period 4.2-3.9 Ga observable on the lunar surface may have disturbed the isotope systematics of the exposed FAS samples. Most of these samples are breccias and often have disturbed Rb-Sr and/or Ar-Ar ages that record ages significantly younger than those obtained using a system like Sm-Nd with a higher closure temperature. Although the Sm-Nd system is considered to be one of the more robust chronometers (Gaffney et al., 2011), open system behaviour in Sm-Nd in some lunar crustal rocks clearly is evident (e.g. 78236: (Carlson and Lugmair, 1981; Edmunson et al., 2009; Nyquist et al., 1981). Additional evidence for Sm-Nd disturbance has been provided by the comparison of ^{147}Sm-^{143}Nd model ages in coexisting plagioclase and pyroxene. Norman et al. (2003) argue that samples showing different model ages calculated for both plagioclase and mafic mineral fractions have been disturbed, possibly by impact metamorphism. Norman et al. (2003) showed that plagioclase model ages present a large scatter, but mafic phases in FAS rock show less scatter and yield an age of 4.46 ± 0.04 Ga.

When $^{142}Nd/^{144}Nd$ ratios are plotted versus Sm/Nd ratios, the FAS whole rocks define a steep correlation over a very narrow range in Sm/Nd ratios (Figure 7). This correlation supports an age of crystallization of FAS rocks during the lifetime of ^{146}Sm. The slope of the regression line considering WR measurements yields a $^{146}Sm/^{144}Sm$

ratio of 0.0061 ± 0.0096 (grey line). The uncertainty on this slope is large enough to encompass essentially any reasonable age for FAS rock formation. The Sm/Nd-^{142}Nd/^{144}Nd regression for 60025 has a lower slope and yields an age of 4394^{+20}_{-17} (using the new decay constant published for ^{146}Sm, $T_{1/2}$= 68 Ma (Kinoshita, 2012), and the solar system initial ^{146}Sm/^{144}Sm ratio of 0.0094 recalculated from the value of Boyet et al. (2010)) or 4318 Ma considering the longer half-life of 103 Ma for ^{146}Sm. Sample 62236 falls on the 60025 internal isochron, whereas 15415 is slightly below but within error of the two 60025 measurements. The FAN 62255 has the lowest ^{142}Nd/^{144}Nd ratio and falls below the 60025 internal isochron. When this sample is not considered in the regression we obtain a ^{146}Sm/^{144}Sm ratio of 0.0039 ± 0.0035 for the remaining samples, which corresponds to an age of 4482^{+233}_{-63} Ma ($T_{1/2}{}^{146}$Sm=68 Ma) or 4452^{+338}_{-95} Ma ($T_{1/2}{}^{146}$Sm=103 Ma), similar within error to the age of 60025. Sample 62255 has a large deficit in ^{142}Nd of -45 ppm relative to the terrestrial standard. The age of this sample has never been determined. In order to develop such a large deficit in ^{142}Nd, this sample must have been formed very early in solar system history. The largest deficits previously reported in ^{142}Nd measured in lunar samples were up to -20 ppm in KREEP-rich samples (Boyet and Carlson, 2007 ; Brandon et al., 2009). So far the oldest Sm-Nd internal isochron age for a FAN has been determined on a noritic anorthosite clast from the lunar breccia 67016. Among the two analyzed splits of 67016, a well defined age of 4.562±0.068 Ga was determined (Alibert et al., 1994). However when the regression is calculated using the Isoplot program (version 3.41b, rev. 16 Nov 2005; (Ludwig, 1991)) ages of 4.566±0.250 Ga (MSWD=3.6) and 4.666±0.056 Ga (MSWD=1.9) are obtained for splits ,328 and ,326, respectively. The result for split ,328 thus is too imprecise to constrain the age of FANs, and the result for split ,326 must be inaccurate because it is older than the solar system and could be induced by small-scale disturbance of the Sm-Nd system in the plagioclase (Alibert et al., 1994). Another FAN dated by ^{147}Sm-^{143}Nd provided an age of 4.43 ± 0.03 Ga (Nyquist et al., (Nyquist et al., 2006) using mineral fragments from a feldspathic breccia clast in the Yamato-86032 lunar meteorite, again, as with 60025, more consistent with a FAN formation age substantially after the formation of the solar system. The geochemical composition of this sample suggests that it comes from a different region than that sampled during the Apollo 16 mission (Yamaguchi et al., 2010).

The available isotopic data for FAS rocks thus do not clearly resolve whether all these samples formed simultaneously by crystallization of a LMO or over an extended interval as suggested by the wide range in internal isochron ages. The lack of variation in $^{182}W/^{184}W$ in lunar metals precludes global differentiation of the Moon prior to 4.50 Ga (Touboul et al., 2007; 2009) thus calling into question very old FAS rock ages such as determined for 67016. The lack of isochronous relationships in figures 6 and 7 does not support simultaneous formation of all the FAS rocks from a common source, but the expected linearity could be affected either by slow cooling (McCallum and O'Brien, 1996) and different excavation times of the different samples from deep in the lunar crust, or alternatively simply reflect disturbance to the Sm-Nd systematics due to shock.

5.2. Initial Nd isotope composition of FAS rocks

Another approach to understand FAS origin is to consider the initial radiogenic isotope composition the samples had at their crystallization age. Because ^{146}Sm was still alive when these samples formed, a correction is required for radiogenic ingrowth to the measured data for both ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd isotope systematics. Correcting the measured values to the correct crystallization age is critical for the interpretation of the initial isotope systematics. In the previous section we discussed the difficulty in determining the age of crystallization for FAS rocks and the question of whether the wide range in internal isochrons available record a prolonged formation interval for FAS rocks, variable cooling rates for rocks stored deep in the crust, or later metamorphic disturbance. Given the large age uncertainty for FAS rocks, the initial ^{142}Nd and ^{143}Nd isotope compositions for the samples studied here have been recalculated for a range of probable ages. These results are presented in figure 7. In 2012 a shorter ^{146}Sm half-life was proposed (68 Ma, (Kinoshita, 2012) instead of the value of 103 Ma determined previously. We have decided to present the initial $^{142}Nd/^{144}Nd$ ratios calculated using the two different decays constants because the results of Kinoshita et al. have been questioned recently by internal $^{146,147}Sm$-$^{142,143}Nd$ isochrons on CAIs (Marks et al., 2013; Borg et al. 2014). For all samples, the initial ^{142}Nd and ^{143}Nd isotope compositions are shown for crystallization ages ranging from 4518 Ga (ΔT=50 Ma represented by the circles) to 4268 Ga (ΔT=300 Ma represented by the arrows). This age interval of 250 Ma

fits the range of ages determined for FAS samples. A timing interval of 50 Ma can be considered as a older limit that corresponds approximately to the age of 67075 (Alibert et al., 1994) and is consistent with ^{182}W measurements (Touboul et al., 2007; 2009). The younger limit is the ^{147}Sm-^{143}Nd age of 62236 (Borg et al., 1999). Since FAS rocks have $^{147}Sm/^{144}Nd$ ratios lower than those of chondrites, their calculated initial $\mu^{142}Nd$ and $\varepsilon^{143}Nd$ increase as the ages get older. In figure 7, the Sm-Nd ages determined for 60025 (Borg et al., 2011) and 62236 (Borg et al., 1999) are indicated by the squares along the appropriate curves. This figure shows that a small variation in the sample age will lead to a significant difference in the calculated initial Nd isotope ratio, with correspondingly large consequences for the interpretation of the initial isotopic composition. For example if we calculate the initial $^{142}Nd/^{144}Nd$ ratio for the 60025 whole rock at 4.367 Ga (the age derived from the ^{147}Sm-^{143}Nd isochron) we obtain an initial $\mu^{142}Nd$ = -18 ppm, equal to the present-day $^{142}Nd/^{144}Nd$ of ordinary chondrites (Boyet and Carlson, 2005) at this time considering the half-life of 68 Ma. Instead if we consider the age determined from the ^{146}Sm-^{142}Nd isochron (4.39 Ga for the ^{146}Sm half-life of 68 Ma), the initial $\mu^{142}Nd$ value changes to +2 ppm. The calculated initial $^{142}Nd/^{144}Nd$ ratios are similarly sensitive to the ^{146}Sm half-life and assumed initial $^{146}Sm/^{144}Sm$. For example, the same calculation quoted above, but using the 103 Ma half life, leads to initial $\mu^{142}Nd$ = +6 ppm at 4.367 Ga and +2 ppm at 4.32 Ga (the ^{146}Sm-^{142}Nd age is different here because of the change of the decay constant).

In the model age evolution diagram shown in figure 7 we have considered 3 different Sm-Nd reference parameters for the bulk Moon: 1) Evolution using the CHUR parameters defined for the ^{147}Sm-^{143}Nd systematics (Bouvier et al., 2008) and the average $^{142}Nd/^{144}Nd$ ratio measured for ordinary chondrites ($\mu^{142}Nd_{today}$=-18 ppm / JNdi-1 standard; (Boyet and Carlson, 2005) in figure 7 A,B; 2) Evolution using the CHUR parameters defined for the ^{147}Sm-^{143}Nd systematics (Bouvier et al., 2008) and the average $^{142}Nd/^{144}Nd$ ratio of enstatite chondrites ($\mu^{142}Nd_{today}$=-10 ppm / JNdi-1 standard; Gannoun et al., 2011) in figure 7 C,D and 3) Evolution using the Sm-Nd parameters defined for the EDR (Early Depleted Reservoir; (Boyet and Carlson, 2005) that is similar to the parameter SCHEM defined by (Caro et al., 2008): $^{147}Sm/^{144}Nd$=0.209 and $\mu^{142}Nd_{today}$= 0 ppm / JNdi-1 standard in figure 7 E,F. The carbonaceous chondrites are not considered because they have nucleosynthetic

anomalies in numerous isotopes (e.g. ^{144}Sm, ^{148}Nd (Andreasen and Sharma, 2006; Carlson et al., 2007)) in comparison to terrestrial and lunar samples suggesting that they have not played a major role in the accretion of the Earth-Moon system.

In all the diagrams presented in figure 7, both the upper left and the bottom right quadrants are not consistent with a coupled evolution of both ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd systematics. A key observation in figure 7 is that the isotopic evolution paths of the FAS rocks do not cross at a single age, hence these data do not provide support for the idea that FAS rocks formed from a single source at a single time. The initial Nd isotopic compositions calculated for 62236 also lie outside of the possible single-stage source evolution curves, but cross these curves at younger ages. Of the samples analysed here, 60025, 62255 and 62236 have ^{142}Nd and ^{143}Nd systematics that can be explained if these three samples derived from a common source over a wide range in time. For example, if the FAS source evolved with chondritic Sm/Nd ratio prior to FAS rock genesis, 62255, 60025 and 62236 provide ^{147}Sm-^{143}Nd model ages of 4.51, 4.42 and 4.11 Ga, respectively. They can produce ^{146}Sm-^{142}Nd model ages that agree with their ^{147}Sm-^{143}Nd model ages if the FAS source has ^{142}Nd/^{144}Nd about 6 (103 Ma half life) to 10 (68 Ma half life) ppm lower than the value calculated from a terrestrial Nd standard such as JNdi-1. A similar lunar initial ^{142}Nd/^{144}Nd has been suggested by Sprung et al. (2013) and Carlson et al. (2014). These results present at least two complications to current models of lunar crustal genesis. First, if the FAS rocks are flotation cumulates from the magma ocean, the range in crystallization and model ages imply that the lunar crust formed over an interval of at least 200 to 400 Ma, and its formation continued past the time when Mg-suite magmas were being intruded deep into the lunar crust (Carlson et al., 2014). A prolonged melting/remelting interval for the lunar crust might be expected if tidal heating of the crust was significant (Meyer et al., 2010). A complication, however, is that the wide range in model ages for the FAS rocks requires that a source with chondritic Sm/Nd ratio be preserved over this interval, but essentially all lunar crustal rocks, including FAS, Mg-suite, and KREEP, have markedly subchondritic Sm/Nd ratios. The initial Nd isotope composition for FAN 15415 cannot be explained by any of these models, as its evolution curve never overlaps the single-stage differentiation curves in the 50-300 Ma timing interval (Figure 7).

559 An alternative to consider is that the source evolution of the FAS rocks was more
560 complicated than a simple one-stage (e.g. chondritic Sm/Nd until their formation)
561 evolution. For example, a super-chondritic composition for the Moon was initially
562 suggested on the basis of positive initial ε^{143}Nd seen for many lunar crustal rocks (e.g.
563 (Carlson and Lugmair, 1988), but more recent results suggest near chondritic to slightly
564 negative initial ε□□□Nd for both FAS rocks (e.g. 60025, Borg et al., 2011) and high-Mg
565 suite rocks (Borg et al., 2013; Carlson et al., 2013). The possibility that the bulk Moon
566 initially had superchondritic Sm/Nd ratios, however, is supported by the ^{146}Sm-^{142}Nd
567 systematics of KREEP and mare basalts. When the ^{146}Sm-^{142}Nd data for KREEP and
568 mare basalts are plotted in a Sm/Nd *vs*. ^{142}Nd/^{144}Nd plot, they define a line that passes
569 above the ^{142}Nd/^{144}Nd value measured for ordinary chondrites at chondritic Sm/Nd
570 ratio (Boyet and Carlson, 2007 ; Brandon et al., 2009). If the Moon started with a
571 ^{142}Nd/^{144}Nd similar to ordinary chondrites, estimates of the ^{147}Sm/^{143}Nd ratio needed to
572 explain the KREEP and mare basalt data are consistent with values suggested for the
573 early Earth's mantle that range from 0.209 to 0.211 (Boyet and Carlson, 2005 ; Carlson
574 and Boyet, 2008 ; Caro et al., 2008). This conclusion, however, depends critically on how
575 much of the variability in ^{142}Nd/^{144}Nd is due to nucleosynthetic causes and not the decay
576 of ^{146}Sm in chrondritic materials. As mentioned previously, if the lunar initial
577 ^{142}Nd/^{144}Nd was about 10 to 14 ppm higher than the average initial ^{142}Nd/^{144}Nd
578 determined for ordinary chondrites, which would be in the range of the average initial
579 ^{142}Nd/^{144}Nd of enstatite chondrites (Gannoun et al., 2011), then at least 62255, 60025
580 and 62236 can be modelled as being derived a source evolving with chondritic Sm/Nd
581 ratio. Chondritic Sm/Nd and Lu/Hf ratios in the bulk-Moon have been proposed recently
582 by Sprung et al. (Sprung et al., 2013) meaning that the ^{142}Nd/^{144}Nd ratio of the lunar
583 mantle would be ~12 ppm higher than that of ordinary chondrites.
584
585 Given the uncertainty in the age of the FAS rocks, figure 8 considers the evolution
586 of their initial Nd isotopic compositions over a range in ages. The initial ^{142}Nd/^{144}Nd
587 ratios for 62236, 60025 and 15415 converge towards a value about 5 ppm below an age
588 corrected JNdi-1 value (assuming chondritic Sm/Nd ratio when back-calculating JNdi
589 evolution) at about 4.47 Ga (ΔT= 100 Ma). This ^{142}Nd/^{144}Nd could be reached starting
590 from an ordinary chondritic initial ^{142}Nd/^{144}Nd assuming a source ^{147}Sm/^{144}Nd ratio of
591 about 0.209, a value suggested for explaining the ^{142}Nd excess measured in terrestrial

592 samples relative to ordinary chondrites (Boyet and Carlson, 2005). Alternatively, if the
593 Moon's initial $^{142}Nd/^{144}Nd$ was closer to the average determined for enstatite chondrites,
594 then this starting point would be reached if the source of FAS samples had a chondritic
595 Sm/Nd ratio between 4.568 and 4.47 Ga. Complicating this explanation, however, is the
596 fact that the Sm/Nd ratios of the FAS rocks are similar, so the evolution of their initial
597 $^{143}Nd/^{144}Nd$ is essentially parallel to one another. What this means is that there is no
598 single time when all of these samples had the same $^{143}Nd/^{144}Nd$. This leaves two the
599 options: (1) that the FANs are derived from a common source, but over a wide (200+
600 Ma) age range, or (2) that their Sm-Nd systematics are disturbed enough to obscure
601 their connection to a single source at a single formation age.
602
603 FAN 62255 has a lower initial $^{142}Nd/^{144}Nd$ ratio compared to other FAS samples
604 measured in this study. In order to reach its very low $^{142}Nd/^{144}Nd$ ratio, this sample
605 must have evolved in a very early-differentiated reservoir characterized by a low Sm/Nd
606 ratio. For example a reservoir formed at 4.568 Ga having a $^{147}Sm/^{144}Nd$ of 0.187 would
607 evolve to the initial $^{142}Nd/^{144}Nd$ ratio calculated for 62255 (deficit of -13 ppm relative
608 to ordinary chondrites at ΔT=150 Ma). An alternative explanation would be that 62255
609 crystallized early in solar system history before other FAS samples analyzed here. The
610 initial ^{142}Nd isotope composition is shown for older ages by the dashed line in figure 8.
611 If this sample crystallized around 60 Ma after the beginning of accretion, its initial
612 $^{142}Nd/^{144}Nd$ ratio would be in agreement with the evolution of a depleted Moon similar
613 in composition to the EDR, or to a Moon with an initial $^{142}Nd/^{144}Nd$ similar to the
614 average of enstatite chondrites. Considering the analytical error on the $^{142}Nd/^{144}Nd$
615 measurement, this timing interval could be reasonably expanded to 100 Ma. In this case
616 the FAN 62255 can be seen as the only FAN analyzed in this study that may have
617 preserved the original signature of the LMO crystallization whereas other FAS rocks
618 have known a more complex history. Among all the samples analyzed in this study, only
619 15415, 62255 and 65315 are classified in the FAN subgroup defined by James et al.
620 (James et al., 1989). Samples 60025 and 62236 are more enriched in mafic phases.
621 Figure 7 shows that the ^{142}Nd-^{143}Nd isotope signatures of 15415 cannot be reconciled
622 with a two-stage model evolution and this may suggest a disturbance of the Sm-Nd
623 systematics after ^{146}Sm became extinct. Argon-Argon ages determined on this sample
624 range widely from 3.9 to 4.1 Ga (Stettler et al., 1973; Turner, 1972) with the 3.9 Ga age,

625 in particular, suggesting that this rock was affected by Imbrium basin formation. No
626 ^{182}W isotope variation has been measured in the FAN 62255 suggesting that this sample
627 crystallized later than 60 Ma after the beginning of the solar system history (Touboul et
628 al., 2009).
629
630
631 *5.3. Earth-Moon relationship*
632 Dating the giant impact that formed the Moon is a difficult task, and although
633 some results in the past suggested a lunar formation age close to the age of the solar
634 system (e.g; Alibert et al., 1984; Kleine et al., 2005), recent studies are more in
635 agreement with a younger age. Results from the short-lived ^{182}Hf-^{182}W chronometer
636 showed that the lunar magma ocean crystallized after the lifetime of ^{182}Hf or no earlier
637 than 60 Ma after the beginning of accretion since in these samples there is no
638 correlation between the Hf/W ratios and the abundance of ^{182}W (Touboul et al., 2007 ;
639 Touboul et al., 2009). The two oldest precise radiometric ages for lunar samples are
640 4.43±0.03 Ga for a feldspathic clast in the lunar meteorite Y-86032 (Sm-Nd by (Nyquist
641 et al., 2006) and 4.417±0.006 Ga for the 6 oldest U-Pb ionprobe spots on a zircon
642 extracted from the matrix of the clast-rich impact melt breccia 72215 (U-Pb (Nemchin et
643 al., 2009). In this zircon, the majority of U-Pb spot ages range down to 4.33 Ga. We
644 consider that the very old age determined for a ferroan noritic anorthosite clast from
645 breccia 67016 (Alibert et al., 1994) cannot be taken as a reference for the age of lunar
646 crust formation (see section 5.1). The younger ages of some FAS rocks from the mafic
647 magnesian sub-group (60025, 62236) suggest that not all FAS rocks formed by
648 plagioclase flotation in the magma ocean in agreement with the conclusion that no single
649 petrogenetic model consistently explains all the characteristics of the various members
650 of the FAS (e.g. Steele and Smith 1973; James 1981; James et al., 1989; Floss et al., 1998).
651 These ages could reflect either later remelting of the lunar interior by impacts, later
652 diapirism of anorthositic mushes from below the crust (Longhi and Ashwal, 1985) or a
653 prolonged time of solidification reflecting tidal heating of the lunar crust due to its
654 proximity to the Earth (Elkins-Tanton et al., 2011).
655 As is the case for lunar chronology, evidence from Earth for the existence of crust
656 prior to ~4.4 is not obvious. The oldest ages for Hadean zircons from western Australia
657 are essentially 4.35 Ga (Cavosie et al., 2007) except for two ion-probe spots dated at 4.4

Ga (Wilde et al., 2001). These ages are similar to the ^{146}Sm-^{142}Nd age for mafic gneisses from the Nuvvuagittuq greenstone belt in Canada (O'Neil et al., 2012). The similar Hf isotopic composition of Hadean terrestrial zircons and lunar zircons (Kemp et al., 2010; Taylor et al., 2009) supports the contemporaneous formation of the crusts on both the Earth and Moon. Different isotope studies suggest, however, that Earth would have experienced successive large-scale differentiation events during its first stages of evolution and prior to the Moon formation. The recent findings of well-resolved ^{182}W excesses measured in a variety of Archean/Hadean terrestrial rocks provides evidence of differentiation events occurring within 50 Ma of solar system formation that were preserved through at least the first 1 to 1.5 Ga of Earth history (Touboul et al., 2012; Willbold et al., 2011). A circa 4.4 Ga age is in agreement with the timing interval for Earth's atmosphere estimated using noble gases (Allègre et al., 1986 ; Mukhopadhyay, 2012). Finally although some debate exists on the initial $^{142}Nd/^{144}Nd$ ratio of the Earth, all models of Earth's accretion based on a mixture of chondrite components would produce an Earth with a ^{142}Nd signature different from that of the modern terrestrial mantle, which then requires a very early differentiation of the silicate Earth in the first few tens of Ma of solar system history, thus before the giant impact event forming the Moon (Boyet and Carlson, 2005). Enstatite chondrites are the closest to the accessible silicate Earth for their $^{142}Nd/^{144}Nd$ ratios, but in average this group still have a resolvable deficit of 10 ppm (Gannoun et al., 2011). The nature of the building blocks making the Earth is still widely controversial. For example, Burkhardt et al. (Burkhardt et al., 2011) showed that the Mo isotope signature of the Earth cannot be reconciled with any combination of chondrites.

6. Conclusion

We present data on ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd systematics measured on several samples from the lunar crust belonging to the FAS group. The samples do not define statistically significant regression lines when they are plotted in isochron diagrams for either the ^{147}Sm-^{143}Nd or ^{146}Sm-^{142}Nd systems. This suggests that they do not have the same crystallization age, they come from different sources, or at least some samples have had their Sm-Nd systematics disturbed by shock metamorphism. Due to its short half-life, the ^{146}Sm-^{142}Nd system is less sensitive to open-system behaviour that

occurred after 4.1 Ga due to the extinction of ^{146}Sm . All FAS rocks have deficits in ^{142}Nd relative to the JNdi-1 terrestrial standard in the range -45 to -15 ppm after correction of secondary neutron capture produced during the cosmic ray exposure of the lunar crust. We have explored the implications of their initial isotopic compositions for crystallisation ages in the range of 50-300 Ma after the beginning of accretion. Evolution models considering both a bulk-Moon with superchondritic Sm/Nd ratio or an initial ^{142}Nd isotope composition similar to that of enstatite chondrites with chondritic Sm/Nd ratio are more consistent with the Sm-Nd data measured on FAS rocks compared to a model considering a bulk-Moon of ordinary chondritic composition. Our results confirm the idea that most FAS rocks are not a primary product of the lunar magma ocean crystallization. 62255, which is classified in the ferroan anorthosite subgroup has the largest deficit in ^{142}Nd and does not appear to have followed the same differentiation path as the other analyzed samples. The ^{142}Nd isotope composition of this sample suggests instead a crystallization age around 60-100 Ma after the beginning of solar system accretion. If so, this sample could be the only FAN so far analyzed for ^{142}Nd that has preserved the direct memory of the lunar magma ocean crystallization and this age would correspond to the age of the giant impact forming the Moon.

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Table 1. Sm isotope composition measured on unspiked samples and terrestrial standards. The difference between terrestrial ratios and those determined in FAS samples is expressed in epsilon notation. Sm isotope ratios have been calculated using two different normalization schemes. Errors are 2σ for standards and $2\sigma/\sqrt{n}$ for samples. The Sm isotope composition of sample 60025 was measured in (Boyet and Carlson, 2007) and no Sm anomaly was found. The Sm isotope composition of 62236 normalized to $^{148}Sm/^{154}Sm$ is presented in Borg et al (1999). This sample has a substantial neutron exposure history with $\varepsilon^{149}Sm$ and $\varepsilon^{150}Sm$ equal to -30.8 and 61.4, respectively.

Table 2. Sm/Nd ratios and Nd isotope composition of FAS samples. Sm/Nd ratios have been measured by isotope dilution. Isotope measurements were performed on the DTM Triton during two periods (sequence 1 and sequence 2 in 2010). $^{142}Nd/^{144}Nd$ ratios were measured using both dynamic and static routines whereas $^{143}Nd/^{144}Nd$ and $^{145}Nd/^{144}Nd$ were measured statically only. Errors are 2σ for standards and $2\sigma/\sqrt{n}$ for samples. The $^{142}Nd/^{144}Nd$ isotope ratios of two samples (15415 and 62236) have been modified by neutron fluence effect and the correction method developed by Rankenburg et al (2006) has been applied (see text).
60025* corresponds to the sample measured by Boyet and Carlson (2007) using the same instrument. For this sample, the $\mu^{142}Nd$ was calculated using the average value for the terrestrial standard during the 2007 study.

Figure caption

Figure 1. Reproducibility of the $^{147}Sm/^{144}Nd$ isotope ratio obtained with different dissolution procedures. Experiments were made on 1 g sample aliquots of a terrestrial anorthosite. Method 1: dissolution in concentrated HF-HNO_3 acids in Teflon beakers (n=4). Method 2: dissolution using a mixture of 66% lithium tetraborate – 33% lithium metaborate. The Sm-Nd isotope tracer was added before the REE co-precipitation with Fe (n=3). Method 3: dissolution using a mixture of 66% lithium tetraborate – 33% lithium metaborate. The Sm-Nd isotope tracer was added after the REE co-precipitation with Fe (n=3).

Figure 2. Influence of cosmic ray produced secondary thermal neutrons on the Sm-Nd isotope composition of lunar samples. A. Sm isotope composition of lunar samples expressed relative to the terrestrial isotope composition (epsilon notation). Effect of neutron capture due to cosmic rays is shown by the ε^{149}Sm-ε^{150}Sm negative correlation. In the FAS samples analyzed in this study, only two samples have ε^{149}Sm abundances different from the terrestrial value: 62236 (measured by Borg et al., 1999) and 15415. The open square corresponds to 15415 and represents εSm values calculated with measured isotope ratios normalized to $^{147}Sm/^{152}Sm = 0.56081$. Using this normalization, sample 15415 does not plot on the correlation line. One explanation is the production of ^{152}Sm caused by neutron capture on ^{151}Eu. Sm isotope ratios have been recalculated using the normalization ratio of $^{148}Sm/^{154}Sm = 0.49419$. Using this calculation, the sample plots on the correlation line. Borg et al. (1999) already considered this effect when they measured 62236 and isotope ratios were normalized to $^{148}Sm/^{154}Sm = 0.49419$. Sm isotope data presented in this paper are all normalized to the $^{148}Sm/^{154}Sm$ ratio. The choice of the normalization ratio has no consequence on mare basalt Sm isotope composition because these samples have low Eu/Sm ratio so the ^{152}Sm production by neutron capture on ^{151}Eu is negligible. B. Correction of the $^{142}Nd/^{144}Nd$ ratio using the measured $^{149}Sm/^{154}Sm$ ratios. In 2007, Boyet and Carlson applied a correction following the equation developed in Nyquist et al., (1995) where the value of 41,000 barns is considered for the tabulated neutron capture cross section. Instead the value of 71,627 barns has been used in Rankenburg et al., (2006) and Brandon et al., (2009). The difference on the corrected $^{142}Nd/^{144}Nd$ ratio using the two methods is significant only for sample 62236 since it is higher than the external reproducibility of 5 ppm on the $^{142}Nd/^{144}Nd$ ratio of the terrestrial JNdi-1 standard.

Figure 3. Comparison of $^{142}Nd/^{144}Nd$ ratios measured in both dynamic and static modes. All data are normalized to the standards reported in Table 2 for each of the distinct analytical campaigns.

Figure 4. 62236 Sm-Nd isochron plot defined in Borg et al., 1999. Our 62236 WR measurement has been added to the figure for comparison. In Borg et al. (1999) Nd isotope were corrected using the $^{146}Nd/^{144}Nd$ ratio of 0.72414 so our measurement plotted in this diagram has been calculated using the same correction scheme. Our WR measurement falls to the right part of their isochron.

Figure 5. ^{147}Sm-^{143}Nd isochron diagram for FAS rocks. The internal isochron published in Borg et al. (2011) is represented by the dotted line. The most radiogenic mineral phase for the 60025 isochron (olivine + pyroxene; $^{147}Sm/^{144}Nd$=0.3) is not shown here. The FAS regression line considers the 5 WR samples (15415, 60025, 62236, 62255, 65135).

Figure 6. ^{146}Sm-^{142}Nd evolution diagram for FAS whole rocks. Results obtained on the FAN 60025 and published by Borg et al. (2011) are shown. We note a $^{142}Nd/^{144}Nd$ vs. $^{144}Sm/^{144}Nd$ correlation for whole rock FANs, however they do not yield a statistically significant isochron.

Figure 7. Coupled $\mu^{142}Nd$-$\varepsilon^{143}Nd$ source models. The initial compositions of the FAS rocks have been recalculated back to different ages ranging from 50 Ma to 300 Ma after the beginning of solar system formation. The age determined on samples 60025 (Borg et al., 2011) and 62236 (Borg et al., 1999) are indicated by the squares. The two upper left and lower right quadrants are not allowed in case of coupled two-stage evolution of both ^{146}Sm-^{142}Nd and ^{147}Sm-^{143}Nd systematics.

A. Differentiation from a mantle with ordinary-chondritic composition ($\mu^{142}Nd_{today}$=-18 ppm / JNdi-1 standard; see (Boyet and Carlson, 2005). ^{147}Sm-^{143}Nd parameters are those defined in Bouvier et al. (2008). Black lines show the evolution of differentiated reservoirs formed during the first 300 Ma of the solar system history. The timing is represented in grey. In black are noted the value of the $^{147}Sm/^{144}Nd$ ratios for the different early-formed reservoirs.

B. Differentiation from a mantle with enstatite-chondritic composition ($\mu^{142}Nd_{today}$=-10 ppm / JNdi-1 standard; see Gannoun et al., 2011). ^{147}Sm-^{143}Nd parameters are those defined in Bouvier et al. (2008).

C. Differentiation from a depleted mantle characterized by a $^{147}Sm/^{144}Nd$ ratio of 0.209 since 4.568 Ga (Boyet and Carlson 2005).

Figure 7. $^{142}Nd/^{144}Nd$ evolution model of the lunar interior. $^{142}Nd/^{144}Nd$ ratios are expressed in ppm values relative to the ordinary chondrite reference (≈ -18 ppm relative to the JNdi-1 terrestrial standard, see (Gannoun et al., 2011). $^{142}Nd/^{144}Nd$ ratios for FAS rocks are recalculated back to different crystallization ages ranging from 150 to 200 Ma after the beginning of solar system formation considering the measured Sm/Nd ratios. The age of 4.36 Ga for 60025 is represented by a square (Borg et al., 2011). 62236 has been recalculated back to younger ages since Borg et al. (1999) have dated this sample at 4.29 Ga (square). The $^{142}Nd/^{144}Nd$ isotope compositions of samples 15415, 60025 and 62236 can be reproduced by a two-stage evolution model considering that the bulk moon evolved with a superchondritic Sm/Nd ratio beginning at 4.568 Ga, then at 100 Ma after the solar system formation, the Moon formed by giant impact and the crystallization of the magma ocean produced a FAS source reservoir characterized by low Sm/Nd ratios ($^{147}Sm/^{144}Nd$ in the range 0.16-018 represented by the grey fields). A lunar magma ocean crystallization at 150 Ma or later cannot be reconciled with the data measured on samples 15415, 60025 and 62255. FAN 62255 has a lower initial $^{142}Nd/^{144}Nd$ ratio compared to other FAS rocks measured in this study and the model proposed here does not fit with this sample suggesting that some FANs have known a different history. The conclusions are similar if we consider that the bulk Moon evolves with an enstatite chondrite Sm-Nd composition during the first stage. In this case the initial ^{142}Nd isotope compositions of samples 15415 and 60025 are best explained for a differentiation event that took place 125 Ma after the beginning of solar system accretion (intercept between the enstatite chondrite line and the light grey field).